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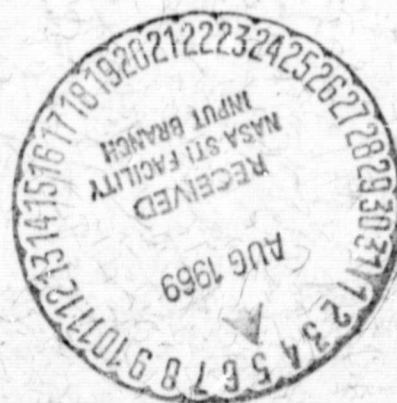
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# ENERGETICS OF HCl AND HF IN VOLCANIC EMANATIONS

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ENERGETICS OF HCl AND HF IN VOLCANIC EMANATIONS

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## ENERGETICS OF HCl AND HF IN VOLCANIC EMANATIONS

### ABSTRACT

Thermochemical data are used to calculate the fugacities of HCl and HF in equilibrium with halogen salts and crystalline silicates. The calculated fugacities are compared with the abundances of HCl and HF in fumarolic gases. Good agreement between the calculated values and the results of hydrothermal experiments is also obtained for HF.

It is found that in the case of fumaroles the abundances of HCl and HF molecules can be explained by assuming some undersaturation of the systems in such crystalline components as NaCl,  $\text{CaSiO}_3$  and  $\text{Al}_2\text{SiO}_5$ . Also the fumarolic gases give evidence that high temperature abundances of HCl and HF are quenched to much lower temperatures recorded at the fumarolic vents.

The relations between HCl and HF and the structure of the silicate melt are also discussed and certain interpretations are given to experimental phase studies.

## ENERGETICS OF HCl AND HF IN VOLCANIC EMANATIONS

### INTRODUCTION

We do not know if most of the chlorine and fluorine at or near Earth's surface was originally deposited there during the birth of the planet or if these constituents gradually came from the interior. However the abundances of HCl and HF in contemporary volcanic emanations point strongly to the second alternative. In fact, it is generally assumed that the abundances of the halogens in Earth's crust and hydrosphere reflect the mechanisms of planetary differentiation (Rubey, 1951).

The acid gases and many other halogen compounds which are continuously emitted from volcanic fumaroles are stable only under high temperature conditions. Analyses of volcanic gases indicate that Cl and F occur predominantly as HCl and HF molecules (Zies, 1929, 1938; White and Waring, 1963). However, these molecules are rapidly precipitated from the atmosphere with water and are destroyed by chemical reactions, and as a consequence normal air contains only undetectable quantities of them.

An interesting contrast to the atmospheric abundances of HCl and HF molecules in Earth's atmosphere is provided by the planet Venus, which may be regarded as an "Earth experiment" run at a higher temperature. Among the spectra of this planet's atmosphere which have been taken from Earth-based telescopes are those

of Connes, Connes, Benedict and Kaplan (1967). These spectra recorded mixing ratios of  $10^{-6.2}$  and  $10^{-8.3}$  for HCl and HF respectively in the Venusian atmosphere but did not record a trace of these constituents in Earth's atmosphere. There is perhaps no other evidence which so dramatically illustrates the differences between hot and cool terrestrial planets.

The relationships of HCl and HF molecules to the magmas from which they are ultimately derived are highly complex and are not easily evaluated in a quantitative way. Also it has been rightly pointed out by White (1957) and by Ellis and Mahon (1964) that the compositions of many thermal waters are probably more closely related to the country rocks than to the magmas from which their thermal energy is derived. Although the relations between the gaseous HCl and HF molecules and the magma are complicated, their relation to solid crystalline phases, either of the magma or of the wall rocks, are simpler and provide a basis for the discussion of the concentrations of these molecules in geologically significant fluid phases. Some of the reactions involved were already discussed by Fenner (1940), Ellis (1957) and Winkler and von Platen (1958). Fenner (1940) also refers to early investigators of HCl-producing reactions. Recently also planetary probe data have made possible the interpretation of Venusian HCl and HF abundances by reactions of this type (Mueller, 1968). In this case the spectrally observed abundances may be interpreted as representing quenched equilibria established between the lower atmospheric gases and the surface rocks at 500-600°K. (Mueller, 1969). We shall see that the situation is somewhat similar

for terrestrial volcanic emanations if account is taken of the character of the magmas and the extensive cooling of these emanations from magmatic temperatures.

#### ABUNDANCES OF HCl AND HF IN FUMAROLIC GASES

Under natural conditions hydrofluoric and hydrochloric acids are common constituents only of gases and fluids which have formed at high temperatures, although in some cases the acid-bearing fluid may have cooled substantially immediately before observation. The result is that although the high temperature HCl and HF abundances may be maintained metastably for a short time, their great reactivity with many mineral compounds assures their rapid disappearance.

The abundances of HCl and HF from some typical fumarolic gases are presented in Tables 1, 2 and 3 in terms of their volume fraction of the total gases. Also shown are the volume percents of the total "active gases" as defined by White and Waring (1963). More complete analyses of three of the Usu gases as given by White and Waring are also shown in Table 4.

The three sets of data shown in Tables 1, 2 and 3 represent emissions from dacitic, rhyolitic and basaltic volcanoes. They were utilized here because of their completeness and because they appear to be of high quality. The Usu analyses in particular appear to be of outstanding quality from the presence in them of only minute quantities of the atmospheric constituents  $N_2$ ,  $O_2$  and Ar (Table 4).

**Table 1**

Gases of Showa-Shinzon, Usu (dacitic) Volcano, Japan (Nemoto, Hayakawa, Takahoshi and Oana, 1957). "Active gases" are defined by White and Waring (1963) as CO<sub>2</sub>, CO, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>, HCl, HF, H<sub>2</sub>S, S, SO<sub>2</sub> and SO<sub>3</sub>. H<sub>2</sub>O comprises from 98.1 to 99.72 of the total gas volume of these samples. The atmospheric contaminants O<sub>2</sub>, N<sub>2</sub> and Ar total less 0.5 percent in all the samples.

Specimen	T°C	Volume Percent Total	Volume fraction × 10 <sup>6</sup> of Total Gases	
		"Active Gases"	HCl	HF
1	760	1.879	358	218
2	525	1.442	207	152
3	220	0.632	214	32
4	655	0.516	448	181
5	750	0.723	390	199
6	700	0.592	510	209
7	645	0.569	490	199
8	464	0.859	130	76
9	460	0.537	569	320
10	430	0.567	667	230
11	328	0.948	140	62
12	300	0.853	150	45
13	203	0.486	718	83
14	194	0.258	120	11
Average			367	144



**Table 2**

**Gases of the Katmai (rhyolitic) Volcano, Alaska (Allee and Zies, 1923).**

**"Active gases" are as defined in Table 1. However CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> were not determined. H<sub>2</sub>O comprises from 99.24 to 99.98 of all the samples (White and Waring, 1963).**

Specimen	T°C	Volume Percent Total "Active Gases"	Volume Fraction $\times 10^6$ of Total Gases	
			HCl	HF
3	400	0.03	261	33
4	400	0.04	88	668
5	350	0.13	884	299
6	300	0.31	2418	403
7	300	0.13	598	546
8	250	0.76	5624	988
9	250	0.10	570	320
10	100	0.02	108	42
11	100	0.02	80	40
Average			1181	314

**Table 3**

Gases of the Kliuchevskii (basaltic) Volcano, Kamchatka (Basharina, 1953a, 1953b; Gorshkov, 1957). "Active gases" are as defined in Table 1.

Large quantities of O<sub>2</sub>, N<sub>2</sub> and Ar are present in the analyses.

Specimen	T°C	Volume Percent Total	Volume Fraction × 10 <sup>6</sup> of Total Gases	
		"Active Gases"	HCl	HF
34	358	0.63	1700	63
35	500	0.81	2511	81
47	270	0.31	496	93
48	296	0.30	630	180
50	490	0.64	320	19
53*	312	0.2	760	0.26
Average			1062	73

Table 4

Chemical analyses of gases of Showa-Shinzon, Usu Volcano,  
Japan in weight parts per million. Reference and specimen  
numbers are the same as for Table 1.

	1	2	3
Temp. °C	760	525	220
SiO <sub>2</sub>	253	289	48
Al	15	14	1.3
Fe	1.3	1.2	5.9
Ca	4.6	4.3	21
Mg	32	14	7.9
Na	22	22	13
K	15	11	1.7
CO <sub>2</sub>	29,200	25,800	13,000
CO	50	34	—
SO <sub>2</sub>	1,490	716	716
SO <sub>3</sub>	21	11	2.7
H <sub>2</sub> S	8.0	42	1,080
S	3.7	1.8	—
Cl	728	420	433
F	238	160	35
Br	1.1	0.9	1.2
B	39	21	5.6
PO <sub>4</sub>	2.8	3.0	0.8
NO <sub>2</sub>	0.01	0.001	0.008
O <sub>2</sub>	51	47	23
H <sub>2</sub>	685	381	20
NH <sub>3</sub>	1.3	0.8	17
N <sub>2</sub>	567	676	1,250
Ar <sup>40</sup>	0.6	—	—

## ABUNDANCES OF Cl AND F IN IGNEOUS ROCKS

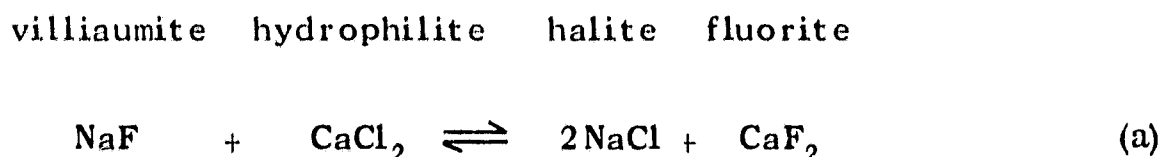
Numerous determinations of Cl and F in igneous and crystalline rocks in general have shown that on the whole F is more abundant than Cl. The data of Koritnig (1951), Behne (1953) and Greenland and Lovering (1966) indicate that in molar terms there is about twice as much F as Cl in igneous rocks. However, individual rocks may show more Cl than F. Also it has been demonstrated by Noble, Vertie, Smith and Peck (1967) that while both Cl and F are lost from glassy silicic volcanic rocks on devitrification, considerably more Cl than F is lost in the process.

In addition to such minerals as fluorite and apatite much of the chlorine and fluorine of crystalline rocks resides in micas and in amphiboles (Gillberg, 1964). Here also fluorine dominates over chlorine. Thus igneous rocks and minerals are quite distinct from volcanic emanations in terms of the F/Cl ratios (Fig. 2). Although this ratio in rocks in part reflects loss on crystallization, it is also possible that it is fundamentally different in magmas and the emitted gases.

## HETEROGENEOUS REACTIONS OF THE ACID GASES

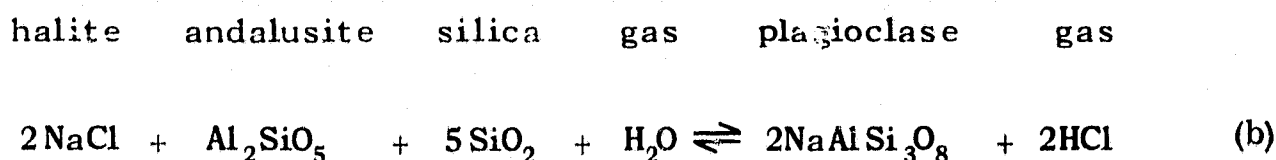
The problem here is to deduce plausible reactions which yield the equilibrium partial pressures of the gases as a function of the temperature, total pressure and compositions of the condensed phases. A comparison may then be made with the results of direct hydrothermal experiments and gas analyses of natural volcanic emanations. In the deduction of suitable reactions it is necessary to

choose the most stable phases for the conditions and for which adequate thermochemical data exist. It is convenient first to select the most stable halogen salts found among the species NaF, CaCl<sub>2</sub>, CaF<sub>2</sub> and NaCl which react with the silicate constituents. Fortunately this choice may easily be made from the reaction



From existing thermochemical data (Kelley, 1960; Robie, 1966 and Wicks and Block, 1963) we find that the standard Gibbs free energy change for this reaction is -23,521 calories at 298°K and -23,710 calories at 1000°K, which indicates that CaF<sub>2</sub> and NaCl are stable relative to NaF and CaCl<sub>2</sub> over a broad range of temperatures. This conclusion is of course also in harmony with the natural occurrences of these minerals (Winchell and Winchell, 1951).

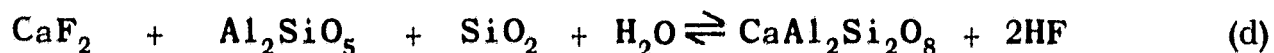
The choice of silicates is somewhat limited by the existing thermochemical data which does not exist for many constituents or which contains large uncertainties. For example, the realistic but complex constituent K Mg<sub>3</sub> AlSi<sub>3</sub> O<sub>10</sub> F<sub>2</sub> (fluorophlogopite) introduces an uncertainty of 2000 calories in the heat of reaction. With these considerations in mind the following reactions may be written:



fluorite   silica   gas   wollastonite   gas



fluorite   andalusite   silica   gas   plagioclase   gas



fluorite   plagioclase   gas   halite   plagioclase



silica   gas



fluorite   plagioclase   gas   wollastonite   andalusite   silica



halite   gas



In these reactions andalusite was utilized rather than other  $\text{Al}_2\text{SiO}_5$  polymorphs because its stability field coincides with the pressures and temperatures over the greatest range of interest (Weill, 1966; Holm and Kleppa, 1966).

It should be observed that reactions (e) and (f) are not independent but may be derived by combining reactions (b), (c) and (d).

For purposes of the analysis it is convenient to write the equations of equilibrium for these reactions as follows:

$$\left( \frac{a_{\text{Ha}}^2 a_{\text{Ad}} a_{\text{Si}}^5}{a_{\text{Ab}}^2} P_{\text{H}_2\text{O}} K_b \right)^{1/2} = P_{\text{HCl}} \quad (1)$$

$$\left( \frac{a_{\text{Fl}} a_{\text{Si}}}{a_{\text{Wo}}} P_{\text{H}_2\text{O}} K_c \right)^{1/2} = P_{\text{HF}} \quad (2)$$

$$\left( \frac{a_{\text{Fl}} a_{\text{Ad}} a_{\text{Si}}}{a_{\text{An}}} P_{\text{H}_2\text{O}} K_d \right)^{1/2} = P_{\text{HF}} \quad (3)$$

$$\left[ \left( \frac{a_{\text{Fl}}}{a_{\text{Si}}^4 a_{\text{Ha}}^2} \right) \left( \frac{a_{\text{Ab}}^2}{a_{\text{An}}} \right) K_e \right]^{1/2} = \frac{P_{\text{HF}}}{P_{\text{HCl}}} \quad (4)$$

$$\left( \frac{a_{\text{Fl}} a_{\text{Ab}}^2}{a_{\text{Wo}} a_{\text{Ha}}^2 a_{\text{Ad}} a_{\text{Si}}^4} K_f \right)^{1/2} = \frac{P_{\text{HF}}}{P_{\text{HCl}}} \quad (5)$$

In these equations  $a$ 's refer to the activities of the mineral components indicated by the subscripts. These have the following meaning: Fl = fluorite, Ha = halite, An = anorthite, Ab = albite, Ad = andalusite, Si = crystalline silica, and wo = wollastonite. The  $P$ 's refer to the fugacities of HCl, HF and  $\text{H}_2\text{O}$ .

It is clear from these equations that if a given component does not occur as a pure phase its activity will be less than unity and that this may have a large effect on the fugacities or fugacity ratios. It is therefore convenient to first consider these equations in the form for which all the components occur as pure phases so that all  $\hat{\phi}$ 's assume values of unity. If in addition, we divide the equations (1) to (3) by  $P_{H_2O}$  we obtain:

$$(P_{H_2O}^{-1} K_b)^{1/2} = \frac{P_{HCl}}{P_{H_2O}} \quad (6)$$

$$(P_{H_2O}^{-1} K_c)^{1/2} = \frac{P_{HF}}{P_{H_2O}} \quad (7)$$

$$(P_{H_2O}^{-1} K_d)^{1/2} = \frac{P_{HF}}{P_{H_2O}} \quad (8)$$

$$K_e^{1/2} = \frac{P_{HF}}{P_{HCl}} \quad (9)$$

$$K_f^{1/2} = \frac{P_{HF}}{P_{HCl}} \quad (10)$$

The equilibrium constants for these equations may be calculated as a function of the temperature by utilizing the previously cited sources of thermochemical



data and the latest sources for the heat of formation of andalusite. Although it is not possible to estimate the uncertainty in the latter value, the results of two different investigators yield closely similar results. Thus Waldbaum (1965) obtained  $\Delta H_{298} = -619,158$  calories while Holm and Kleppa (1966) obtained  $-619,390$  calories. The values of  $\log K_b$ ,  $\log K_c$  and  $\log K_d$  are listed in Table 5 as a function of the temperature.

Table 5

Logarithms of the equilibrium constants of halogen gas-producing reactions. Sources of the thermochemical data are Kelley (1960), Wicks and Block (1963), Robie (1966), Holm and Kleppa (1966) and Waldbaum (1965).

T°K	$\log K_b$	$\log K_c$	$\log K_d$
298	-20.2	-27.4	-26.4
400	-13.0	-18.7	-17.6
500	-8.85	-13.6	-12.5
600	-6.14	-10.2	-9.15
700	-4.24	-7.83	-6.75
800	-2.88	-6.03	-4.98
900	-1.85	-4.64	-3.62
1000	-1.08	-3.55	-2.54
1100	-0.514	-2.67	-1.66
1200	-0.219	-1.94	-0.926

If we set  $P_{\text{H}_2\text{O}} = 1 \text{ atm}$  we obtain the plots of Fig. 1 corresponding to reactions (b), (c) and (d) and in which  $\log P_{\text{HCl}}$  and  $\log P_{\text{HF}}$  are shown as a function of  $1/T$ . On curve (b) the discontinuity corresponding to the fusion of pure NaCl is apparent. The effect of increased water fugacity, such as might correspond to increased depth below the surface may also be seen from Fig. 1. Although little is known of the detailed mixing properties of HCl, HF and  $\text{H}_2\text{O}$  under these conditions, it may be assumed as a first approximation that  $P_{\text{HCl}}/P_{\text{H}_2\text{O}}$  and  $P_{\text{HF}}/P_{\text{H}_2\text{O}}$  are equal to the mole fractions of these gases. Then since these ratios vary as  $P_{\text{H}_2\text{O}}^{-1/2}$  each order of magnitude increase in the water fugacity shifts the curves to the right by  $1/2$  unit but decreases  $\log (P_g/P_{\text{H}_2\text{O}})$  by this amount.

The equilibrium constants for reactions (e) and (f) may be obtained from (b), (c) and (d) (Table 5). The gaseous ratios corresponding to equation (9) and (10) are plotted in Fig. 2 as curves e and f. It is clear that these curves are separated by the free energy of formation of anorthite from wollastonite and andalusite which is of the order of -1500 calories. Although the latter value is consistent with the observation that anorthite is the stable phase, the precise value of the free energy change has an uncertainty as large as its magnitude so that the exact value of the separation of these curves is probably not significant.

A test of equation (7) is provided by some experimental data presented by Ellis and Mahon (1964). They investigated the solubility of fluorite in nearly pure water at temperatures ranging from 125–350°C. Especially pertinent here

is their determination of the fluorite solubility in the presence of amorphous silica. They in fact observed that the concentration of F was considerably increased relative to Ca by the presence of the silica and attributed this to incongruent solution by reaction (c). Unfortunately Ellis and Mahon give neither the time scale nor the crystalline products (if any) of their runs. It is interesting however to consider the possibility that the runs may have been close to saturation with the stable mineral phases quartz and wollastonite in addition to fluorite; for if this is the case the F concentration should be close to that predicted by equation (7).

According to Ellis and Mahon (1964) at 300°C the liquid phase with  $\text{CaF}_2$  and amorphous silica added contained approximately 8.5 ppm F. If this is regarded as HF it is equivalent approximately to  $\text{HF}/\text{H}_2\text{O}$ . To compare this with equation (7) we must first determine HF in the vapor phase. We may do this by an easy extrapolation of the data to the critical temperature of water at 374°C and 218 atm where the concentration of HF in the liquid and vapor phase is the same. We then find that the concentration of HF is about 8 ppm or if we convert to approximate fugacity ratios:

$$\frac{P_{\text{HF}}}{P_{\text{H}_2\text{O}}} = 10^{-5.1}$$

At this temperature and pressure the fugacity coefficient of water is 0.65 (Klotz, 1950). If we then utilize  $K_e$  and Fig. 1 we obtain the thermochemical value

$$\frac{P_{\text{HF}}}{P_{\text{H}_2\text{O}}} = 10^{-5.6}$$

Since this calculation ignores the possible deviation of HF from ideality and embodies all the uncertainties of the thermochemical data the agreement with Ellis and Mahon's (1964) result is remarkably good. This agreement of course also supports the postulated near saturation of their runs with crystalline quartz and wollastonite.

Although the simplified equation (7) is in harmony with the results of the hydrothermal experiment, the interpretation of the fumarolic gas compositions is less straightforward. In this case the general equations (1) to (5) are required.

We note first of all that magmas are not generally saturated with some of the components which enter into the reactions. Thus NaCl,  $\text{Al}_2\text{SiO}_5$  and  $\text{CaSiO}_3$  are rare or unknown primary precipitates of magmas, although crystalline NaCl is a late precipitate of magmatic fluids trapped as inclusions (Roedder and Coombs, 1967). Also the plagioclase constituents usually occur as solid solution components rather than as pure phases. In the case of  $\text{CaF}_2$  little or no information is available for fine grained volcanic rocks, although its common occurrence in acidic plutonic rocks makes it seem likely that it is a primary phase on the solidus. The net result of these considerations is that the activities which appear in equations (1) to (5) will be reduced an unknown amount below the values of unity implied in equations (6) to (10). A qualitative assessment of these effects can however be made.

In the case of plagioclase the effect of solid solution should not be very great provided the crystals approach ideal solutions and provided they do not differ by a factor of two or so from  $An_{40}$ . Although the plagioclase solid may be far from ideal at low temperatures the data of Bowen (1928) indicate that at high temperatures their behavior is nearly ideal. We shall assume the latter behavior for solidus temperatures. We may illustrate the effect of plagioclase first for equation (4): For acid to intermediate rocks the plagioclase does not differ greatly from  $X_{Ab} = 0.6$  where  $X_{Ab}$  is the mole fraction of the albite component. But if  $X_{Ab} = Q_{Ab}$  then

$$X_{Ab}^2 = (0.615)^2 = 0.385 = X_{An}$$

so that the ratio  $Q_{Ab}^2/Q_{An}$  will be near unity. Also equations (1) and (5) will be affected only by factors of  $1/0.6$  and  $0.6$  respectively. Equation (3) will be affected by a factor of  $1/0.6$ . It is clear from the equations then that in general the values of the acid gas fugacities of equation (1) to (3) should be reduced from the values given by equations (6) to (8) and that this reduction should come about through the reduction of  $Q_{Ha}$ ,  $Q_{Ad}$  and  $Q_{F1}$ . In the case of silica undersaturated magmas they are also reduced through  $Q_{Si}$ . In the case of equations (4) to (5) the effect should be largely to increase the ratio  $P_{HF}/P_{HCl}$  over the values predicted by equations (9) and (10) and curves c and f of Fig. 2.

Examination of Tables 1, 2 and 3 and of Fig. 2 shows that the features expected from the analysis of equations (1) to (5) are shown by the fumarolic gases. All the observed values of HCl and HF fall in the range of 10 to some thousands of ppm. It is clear that if the simple equations (6) to (10) held such low values of HCl could correspond only to temperatures far lower than those associated with magmatism or of the highest recorded values of the gases. Furthermore at such low temperatures the concentrations of HCl and HF should differ greatly as is shown by Fig. 1.

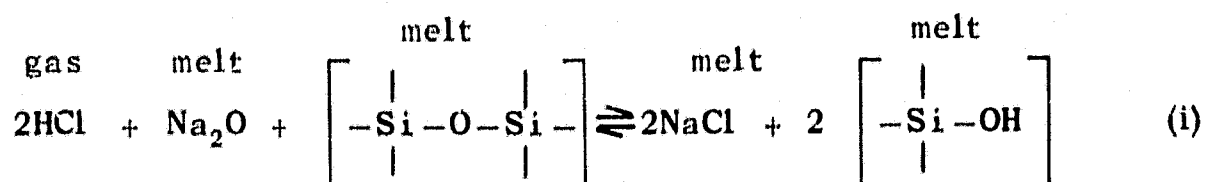
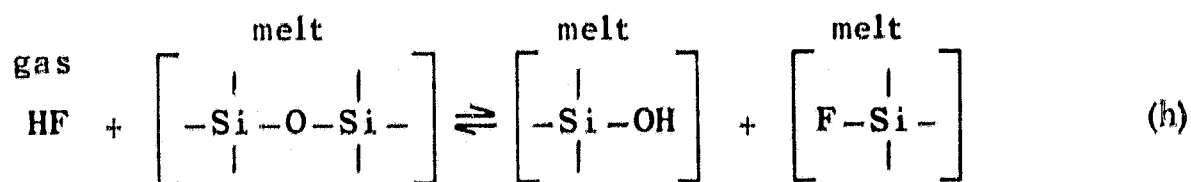
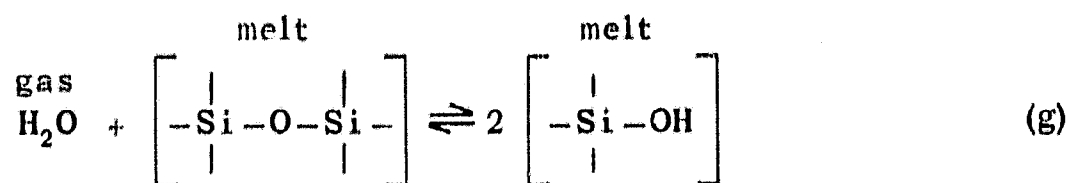
The major trend of the cooled fumarolic gases is traced by the full curve to the right of curves e and f. It is especially well-defined for the high quality Usu gas analyses and indicates that there is only a modest decrease in the HF/HCl ratio over a temperature drop of more than 500°C. Of particular interest is the convergence of this trend and the reaction curves at temperatures in the range of typical lava temperatures (1200-1300°K). The slight displacement of the trend to the right of these curves is attributable to the lower solid component activities as previously discussed.

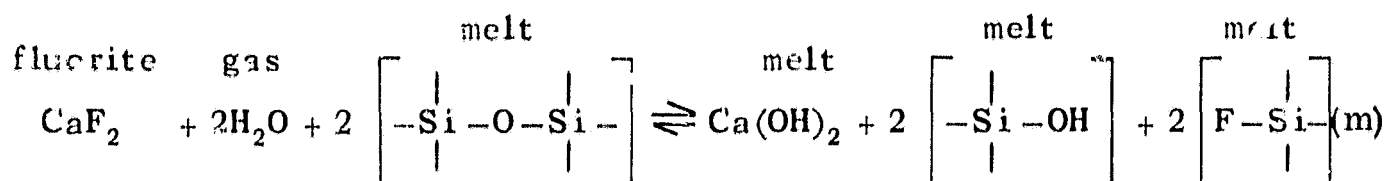
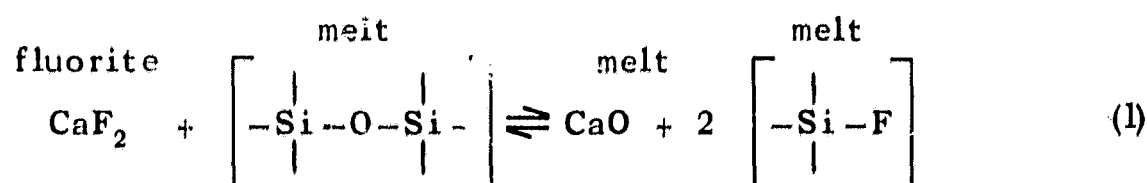
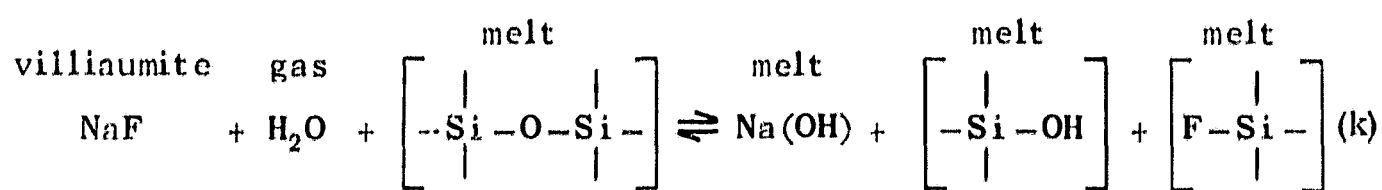
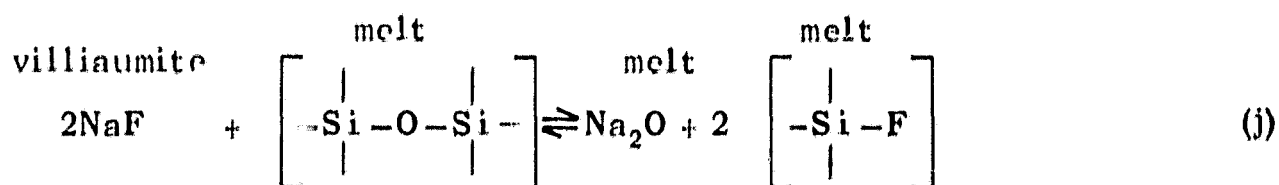
It thus seems likely that although equilibrium between the gases and the condensed magmatic phases is established at liquidus temperatures, the gases are effectively quenched as they find egress to the surface and this results in the retention of the high temperature HF/HCl ratios even after substantial cooling.

As mentioned previously, the abundances of the volcanic gases may also be governed by reactions with mineral phases of the wall rock. Although it would be difficult to distinguish this case from equilibria involving crystalline magmatic phases, we may say that if such reactions are represented here they must have occurred at close to magmatic temperatures.

#### RELATION OF THE ACID GASES TO SILICATE MELTS

Although heterogeneous equilibria may be established at high temperatures between the halogen gases and crystalline phases of the magma or wall rock, the ultimate source of most of the halogens is the silicate melt. From experimental evidence of the effect of halogen compounds on silicate liquidus temperatures and on melt viscosities, and from the similar behavior of water, certain reactions are suggested. Some of these are as follows:





In writing these reactions an attempt is made only to show the possible effect of  $\text{H}_2\text{O}$ , H and F on the Si-O-Si bridges, but no attempt is made to further characterize such species as Na, Cl, Ca, etc in the melt. It is not implied for example that NaCl,  $\text{Na}_2\text{O}$ , CaO, Na(OH), and  $\text{Ca}(\text{OH})_2$  occur as such in the melt. Although none of these reactions has been verified directly, these solubility and viscosity data may be interpreted as resulting from them or from analogous reactions. For example, the profound effect of water on the viscosity of melts of granitic composition is well known (Shaw, 1965). Although the structure of such melts is



still only poorly known it is reasonable that both the decrease in liquidus temperatures and viscosity are attributable to reactions such as (g) in which the Si-O-Si bridges are destroyed by reaction with water (Wasserburg, 1957).

The strong reaction of HF and HCl with silicous silicate melts is shown by the work of Wyllie and Tuttle (1964). They found that an aqueous solution containing 5 weight percent HF at 2750 bars lowered both the albite and granite solidus temperatures profoundly relative to pure water at the same pressure. However, although HCl lowered the solidus temperature of albite it raised that of granite. This shows that although reaction (h) may occur in the presence of HF, the behavior of HCl must be considered in relation to NaCl.

Although NaF-bearing systems are rare in nature the experimental work of Koster van Groos (1966) and of Koster van Groos and Wyllie (1968) on systems containing this constituent and NaCl further clarify the behavior of halogens in melts. Here again NaF strongly lowers the liquidus temperatures of the system albite-H<sub>2</sub>O. The accompanying marked decrease in viscosity points to the disruption of the Si-O-Si bridges as in reactions (j) and (k). Furthermore reaction (k) also suggests a mechanism for the greatly enhanced solubility of water in this system.

The reactivity of NaF in the system albite-H<sub>2</sub>O is not duplicated by NaCl. In this case both the lowering of the liquidus temperatures and the solubility of NaCl are restricted. Furthermore, according to Koster van Groos (1966)

the effect of NaCl on the viscosity of albite liquids is very small. This indicates that the NaCl equivalent of reaction (j) probably does not occur. However NaCl does markedly increase the solubility of water in albite melts.

The behavior of HCl as reported by Wyllie and Tuttle (1964) is somewhat clarified by the results of Koster von Groos and the reactions presented here (Fig. 1). First, although both H and F probably react strongly with the Si-O-Si bridges, in the case of HCl only H reacts in this way. But Fig. 1 shows that significant HCl is present only at high temperatures and that at lower temperatures it is replaced by relatively unreactive NaCl. Thus the difference in behavior of the albite and granite solidus relative to HCl may be interpreted as a thermal effect. At the lower temperature of the granite solidus HCl reacts quickly to form the poorly soluble NaCl.

By analogy with reactions (j) and (k) it seems likely that the more common constituent  $\text{CaF}_2$  will also react strongly with the bridging Si-O-Si chains of the melt; (l) and (m) are two suggested reactions. Indeed some evidence for reaction (l) appears in the results of Weymouth and Williamson (1957) who found that on heating a granite under essentially anhydrous conditions melting began between grains of fluorite and alkali feldspar and muscovite in the temperature range of 800 to 900°C.

In the case of fumaroles it is likely that most HCl and HF results from the displacement to the left, with falling pressure, of reactions such as (h) and (i).

However to the degree that equilibrium is maintained with the solids, reactions such as (b) to (f) will also be simultaneously valid. An important point of reactions (h) and (i) is that the forms in which halogens occur in the gas phase is probably quite different from their forms within the melt. At equilibrium the molecular distribution depends only on the temperature, pressure and bulk composition of the system.

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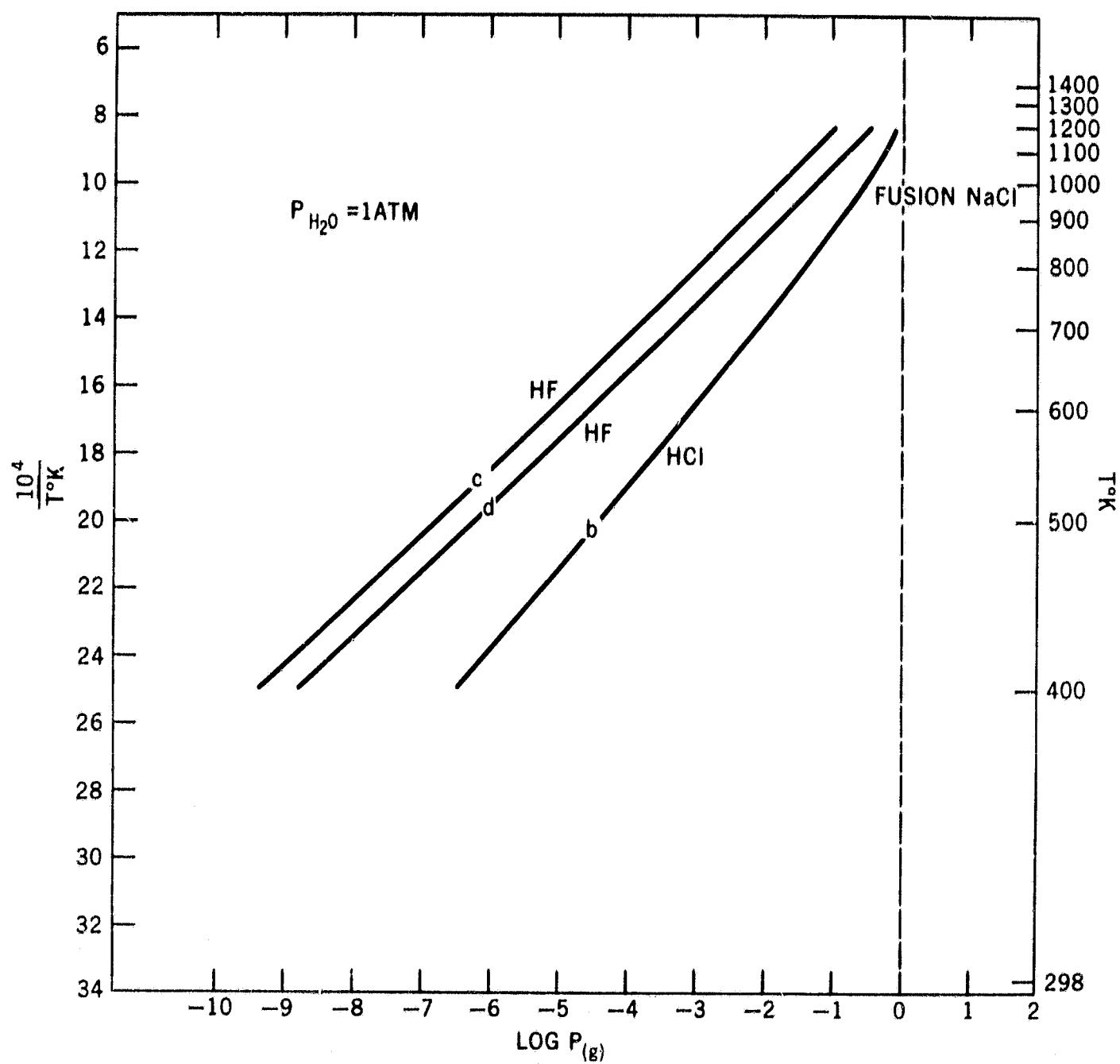


Figure 1. Logarithms of the gas fugacities of HCl and HF as a function of temperature and at unit fugacities of water and solid constituents. The curves, with letters referring to the corresponding reactions (see text), were calculated from thermochemical data.

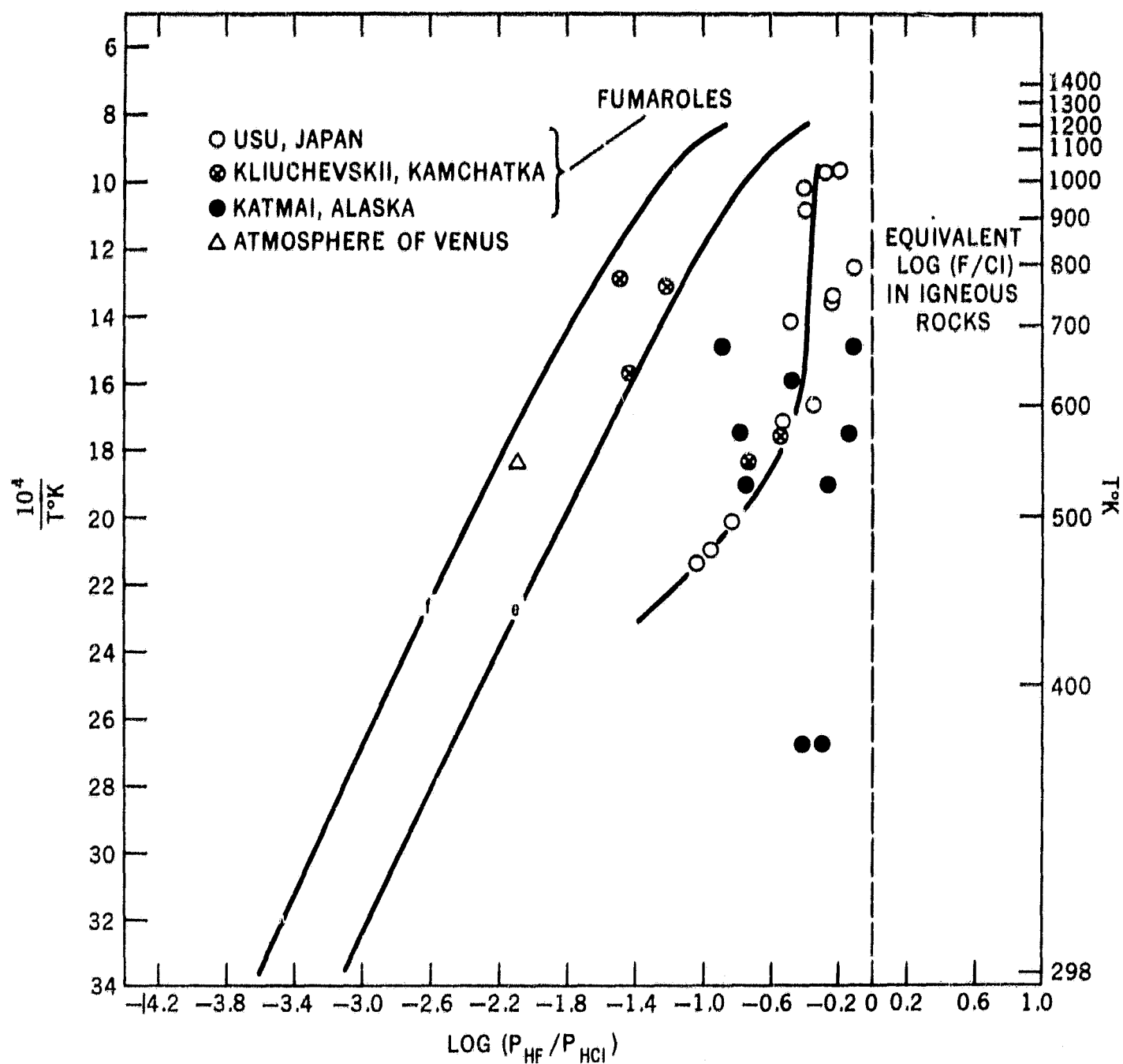


Figure 2. Logarithms of the fugacity ratios  $P_{\text{HF}}/P_{\text{HCl}}$  and the abundance ratios  $\text{HF}/\text{HCl}$  as a function of the temperature. The fugacity ratios represented by curves e and f were calculated from thermochemical data and correspond to reactions (e) and (f). The data points represent the  $\text{HF}/\text{HCl}$  abundance ratios from fumaroles and are here assumed to be the same as the fugacity ratios. The corresponding value for the Venusian atmosphere (Mueller, 1968) is also plotted. It may be noted that the normal range of the equivalent  $\text{HF}/\text{HCl}$  ratio for igneous rocks falls to the right of the unit ratio line which is dashed.